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# Oxygen-17 Dynamic Nuclear Polarisation Enhanced Solid-State NMR Spectroscopy at 18.8 T

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**We report $^{17}$O Dynamic Nuclear Polarisation (DNP) enhanced solid-state NMR experiments at 18.8 T. Several formulations were investigated on the $Mg(OH)_2$ compound. A signal enhancement factor of 17 could be obtained when the solid particles are incorporated in a glassy *o*-terphenyl matrix doped with BDPA using the Overhauser polarisation transfer scheme whilst the cross effect mechanism enabled by TEKPol yielded a slightly lower enhancement but more time efficient data acquisition.**

Solid-state nuclear magnetic resonance (NMR) spectroscopy involving quadrupolar nuclei, which account for more than 75% of all active nuclei, has become an essential analytical technique for the atomic-scale characterization of a wide range of inorganic, hybrid and organic materials such as glasses, zeolites, surface catalysts, metal-organic frameworks, battery materials or pharmaceuticals to name but a few.[1–4] While for spin I = 1/2 nuclei, the dipolar and chemical shift anisotropy (CSA) interactions are fully averaged out by magic angle spinning (MAS),[5] producing sharp lines positioned at the isotopic chemical shifts, the second-order quadrupolar interaction observed for spin I > 1/2 is not fully removed by MAS,[6–8] yielding field-dependent shifts and broadened NMR lines. These are some of the major limitations to the widespread applicability of quadrupolar NMR.[7–10] The second-order quadrupolar broadening is inversely proportional to the strength of the external field $B_0$ and therefore very high magnetic fields allow high spectral resolution.[11] In parallel, a range of NMR experiments have been designed to completely average out the second-order broadenings. They are based on technically challenging NMR probes permitting sample Double Rotation (DOR)[12] or Dynamic Angle Spinning (DAS),[13] or consist in combining conventional MAS with the manipulation of the different nuclear spin transitions in techniques such as Multiple Quantum MAS (MQMAS)[14] and Satellite Transition MAS (STMAS)[15]. Despite these sophisticated approaches and the increasing availability of high magnetic fields, the sensitivity of quadrupolar NMR remains often low for nuclei of poor natural abundance and/or of low gyromagnetic ratio $\gamma$, requiring prohibitively long experimental times (days) and/or expensive isotopic enrichment.

A spectacular approach to increase the solid-state NMR sensitivity is dynamic nuclear polarisation (DNP)[16,17], which involves the microwave-driven transfer of the large polarization of unpaired electrons[18–21] (*e.g.* added to the samples as paramagnetic polarising agents)[22–28] to the surrounding nuclei in a glass-forming matrix at cryogenic temperatures, typically 100 K or below.[29,30] The drastic signal enhancements permitted by DNP have opened up ground breaking applications on an ever increasing range of systems[31–37] and the approach has been reviewed recently.[38–42] Recent developments have extended the temperature range at which the experiments can be conducted (> 200 K).[24,43,44] One of the biggest drawbacks to MAS DNP at high magnetic fields results from the unfavorable evolution of the NMR signal enhancements with $B_0$ which scales as $B_0^{-1}$ and $B_0^{-2}$ for the two most common polarization transfer mechanisms, cross effect (CE) and solid effect, respectively. However, large signal enhancements (> 80) have recently been obtained at 18.8 T using the Overhauser effect (OE) DNP mechanism[16,44,45] and the narrow-line 1,3-bisdiphenylene-2-phenylallyl (BDPA) radical.[46] The apparent linear scaling of the OE signal enhancement with $B_0$ currently represents one of the most attractive approaches for DNP at very high fields and is an exciting opportunity for quadrupolar nuclei.

A quadrupolar nucleus of particular interest is $^{17}$O due to the ubiquity of oxygen in materials chemistry and biochemistry. However, its extremely low natural abundance (0.037%) makes its NMR detection near impossible unless samples are $^{17}$O-enriched.[47] The feasibility of MAS DNP on $^{17}$O has been recently reported.[48–52] In particular, we demonstrated that high S/N natural abundance $^{17}$O cross polarization (CP) MAS NMR spectra could be obtained on nanoparticles,[49] while more recently, the detection of $^{17}$O DNP NMR spectra of surface hydroxyl sites on mesoporous silica at natural abundance was reported.[52] All these experiments were recorded at 9.4 T and relied on the CE mechanism with bTbk[23] or TEKPol[24] radicals in tetrachloroethane (TCE)[53] as a polarising agent.

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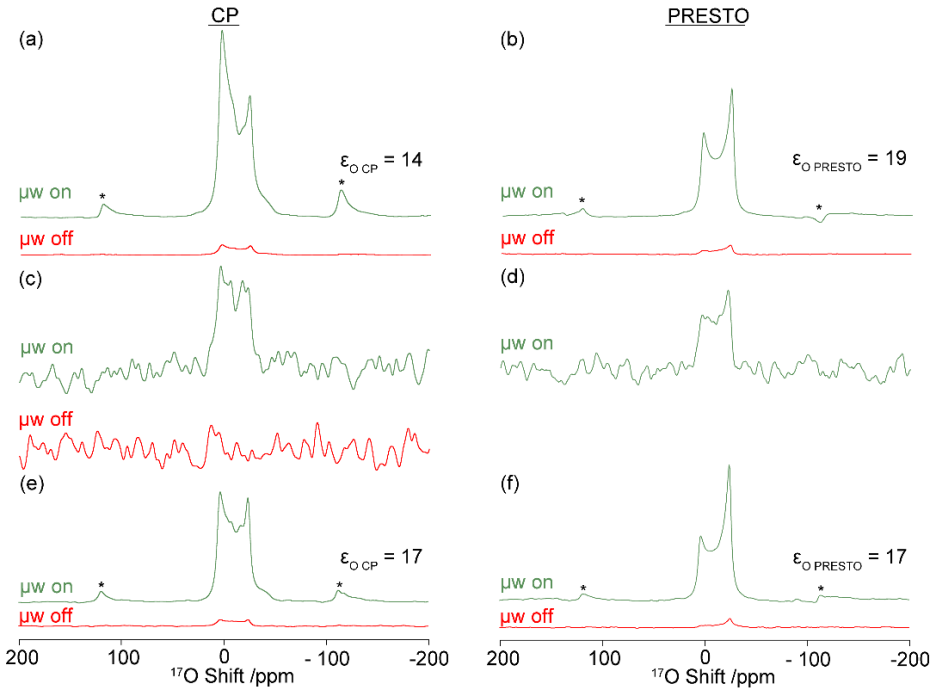


**Figure 1**. (a-d) $^{17}$O CE and (e, f) $^{17}$O OE MAS DNP at 18.8 T. CP (left column) and PRESTO (right column) spectra of Mg($^{17}$OH)$_2$ (a, b, e, f) and natural abundance Mg(OH)$_2$ (c, d) have been recorded at $\nu_0$($^1$H) = 800.130 MHz for CE and at $\nu_0$($^1$H) = 800.215 MHz for OE with microwave irradiation (μw) at $\nu_0$(e-) = 527 GHz (green) at T = 131 K and without μw (red) at T = 115 K. For CE, both samples were impregnated with 16 mM TEKPol in TCE and paramagnetic $O_2$ removed by freeze-thaw cycles (see section 1 in SI for details). For OE, the sample was prepared with a matrix containing 1.4 wt%. BPDA in 90:10 OTP-$d_{14}$:OTP and five freeze-melt cycles (see SI). Spectra (a, b), (c, d) and (e, f) are plotted in absolute intensity. The μw off PRESTO Hahn echo spectrum of Mg(OH)$_2$ was not recorded. Asterisks (*) denote spinning sidebands.

Here, we show that DNP can be applied to efficiently enhance the $^{17}$O MAS NMR signal of Mg(OH)$_2$ in a glassy matrix at 18.8 T, via both the CE and OE mechanisms. We show that CE DNP (using TEKPol/TCE) gives enhancements up to $\varepsilon_{O\ CP}$ = 14, and allows for the fast acquisition of the $^{17}$O spectrum of Mg(OH)$_2$ at natural abundance. Similarly, using the OE scheme, we demonstrate that polarization can be transferred from BDPA in a glassy matrix (10% *o*-terphenyl (OTP), 90% *o*-terphenyl-$d_{14}$ (OTP-$d_{14}$)) to Mg(OH)$_2$ with excellent efficiency, giving enhancements of $\varepsilon_{O\ CP}$ = 17. Both CP[13,54] and PRESTO-II[55] (herein referred to as PRESTO) experiments are reported.

Figure 1a shows the 18.8 T DNP enhanced $^{17}$O MAS NMR of $^{17}$O enriched Mg(OH)$_2$ (*i.e.* Mg($^{17}$OH)$_2$), impregnated with TEKPol in TCE under the CE condition at $\nu_0$($^1$H) = 800.130 MHz. The $^1$H enhancement obtained on TCE ($\varepsilon_H$ = 23) is transferred to the protons of Mg($^{17}$OH)$_2$ via spin diffusion and subsequently to the $^{17}$O nuclei via a selective CP Hahn echo to yield a maximum signal enhancement of $\varepsilon_{O\ CP}$ = 14. In an attempt to be more representative in evaluating the increase in NMR signal with DNP, we have estimated an overall DNP gain $\Sigma^{\dagger}_{O\ CP}$ (see sections S2 of the SI for calculations details)[29,41,56–58] to compare the benefit of 18.8 T DNP vs standard NMR at 18.8 and 9.4 T. The $\varepsilon_{O\ CP}$ = 14 of TEKPol in a TCE matrix translates to a $\Sigma^{\dagger}_{O\ CP}$ of 72 at 18.8 T (Table 1), demonstrating substantial CE DNP efficiency despite the $B_0^{-1}$ dependency of CE. It is worth noting that on freshly prepared samples lower enhancements were observed ($\varepsilon_H$ = 16, $\varepsilon_{O\ CP}$ = 9) and that the maximum values reported above were obtained after holding the sample at 253 K for 20 h before freeze-thaw cycling (see SI) and inserting in to the probe (Figures 1 and S4).

It was recently shown that the use of a PRESTO (phase-shifted recoupling effects a smooth transfer of order) sequence[55] is more efficient for the $^1$H-$^{17}$O heteronuclear polarization transfer and yields for Mg(OH)$_2$, Ca(OH)$_2$ and silica surface[52] line-shapes closer to simulations than with CP, including in the context of MAS DNP.[59] Figure 1b shows the corresponding CE DNP $^{17}$O PRESTO spectra on the same Mg($^{17}$OH)$_2$ sample at 18.8 T. A maximum signal enhancement of $\varepsilon_{O\ PRESTO}$ = 19 was obtained and is slightly higher than $\varepsilon_{O\ CP}$ (14). However, in our hands and at 18.8 T, the overall signal intensity is lower than with $^{17}$O CP as predicted.[55] We also note the asymmetric line shape and dephased spinning side bands are exacerbated by the addition of microwave irradiation (Figure S3). The lower intensity of PRESTO vs CP and line shape disparity is also observed using OE (Figure 1e-f). The $^{17}$O signal enhancement factors obtained open the way to obtain natural abundance spectra using CE at 18.8 T, and we were able to record $^{17}$O CP and PRESTO MAS NMR spectra of Mg(OH)$_2$ relatively quickly in 82 minutes (Figure 1c-d), while the corresponding microwave off spectra show no signal (Figure 1c).

Sample formulation is essential to achieve high DNP enhancement factors, and in particular the choice of the solvent is often critical.[60] It has been shown that OTP forms a highly effective glassy matrix[61] and could be polarized by CE DNP with TEKPol and even more efficiently by OE DNP with BDPA.[44,45,61] In the next paragraphs, we report $^{17}$O enhancement factors using OTP with both TEKPol and BDPA as the polarising matrix. The Mg($^{17}$OH)$_2$ samples were prepared by grinding them within a mixture of protonated and fully deuterated OTP of various ratio containing TEKPol or BDPA radicals (1.3-1.4 wt% equivalent to 34 mM electron spins) followed by multiple cycles (typically 5) between a melt at ~ 343 K[61] and a frozen state at 77 K (in

liquid $N_2$) before the melt is inserted into the precooled NMR probe at ~ 115 K (see SI section S1 for detailed sample preparation).

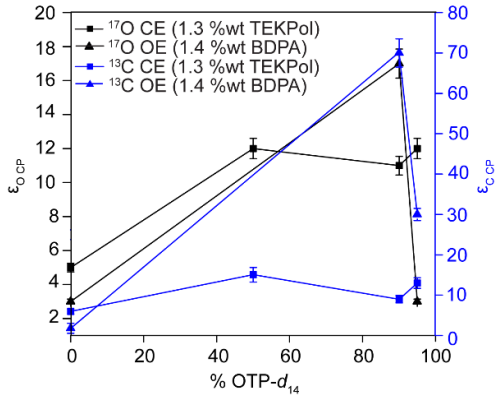


**Figure 2**. $\varepsilon_{O\,CP}$ (black) and $\varepsilon_{C\,CP}$ (blue) measured on Mg($^{17}$OH)$_2$ and OTP matrix (with radical and concentration in brackets) at both CE (triangle) and OE (square) magnetic field strength $B_0$ positions as a function of the OTP-$d_{14}$ component of the OTP matrix.

Figure 2 plots the $^{13}$C and $^{17}$O CPMAS CE DNP signal enhancements of the Mg($^{17}$OH)$_2$/TEKPol/OTP glass matrix as a function of the percentage of OTP-$d_{14}$. The $^{13}$C and $^{17}$O enhancements correspond to the NMR signal amplification of respectively the OTP matrix and the Mg($^{17}$OH)$_2$ particles. The data show that with a fully protonated OTP matrix, the signal enhancements are similar ($\varepsilon_{C\,CP}$ = 8 and $\varepsilon_{O\,CP}$ = 6) revealing that the polarization is efficiently transferred from the glassy matrix to Mg($^{17}$OH)$_2$ and that the polarization is evenly distributed across the particles by $^1$H-$^1$H spin diffusion mechanisms.[63] However, the enhancements are lower than with >50% OTP-$d_{14}$ matrices (vide infra) and is due to both the large size of the $^1$H bath and the short $^1$H polarization time $\tau_{DNP}$ (~ 3 s) yielding a fast decay of the enhanced polarization by relaxation before it can be transferred to Mg($^{17}$OH)$_2$. Increasing the content of OTP-$d_{14}$ in the matrix improves the signal enhancements of the sample (Table 1, Figure S2), in agreement with previous literature showing that deuteration improves DNP enhancements,[60,64] due to the decrease in $^1$H-$^1$H spin diffusion and associated longer $^1$H $\tau_{DNP}$ (~ 31 s). This increase in enhancement plateaued by $\varepsilon_{O\,CP}$ after 50 % OTP-$d_{14}$ and dropped off beyond 90 % OTP-$d_{14}$ in $\Sigma^{+}_{O\,CP}$ suggesting that for CE with TEKPol/OTP at 18.8 T, a 90:10 mixture of OTP-$d_{14}$ and OTP may be optimal for signal to noise per unit time per unit weight.

Figure 2 also displays the $^{13}$C and $^{17}$O DNP signal enhancements at the OE condition of Mg($^{17}$OH)$_2$ prepared in an OTP matrix (with various concentration of OTP-$d_{14}$) and using monoradical BDPA as polarising agent, providing a comparison between CE and OE mechanisms at 18.8 T. At 90:10 OTP-$d_{14}$:OTP, large matrix enhancements are observed ($\varepsilon_H$ = 44, $\varepsilon_{C\,CP}$ = 71), and subsequently the $^{17}$O enhancement of Mg($^{17}$OH)$_2$ ($\varepsilon_{O\,CP}$ = 17, Figures 1e and 2) is substantially larger than with BDPA in a TCE matrix ($\varepsilon_{O\,CP}$ = 5, Figure S5). The multiple freeze melt cycles appear to improve the quality of the glassy matrix, and thus improve the enhancement values on the OTP matrix and sample, compared to directly inserting the sample to the probe (Figure S5). Contrary to the results observed at CE with TEKPol, a further increase in OTP-$d_{14}$ concentration to 95% yields a decrease in matrix enhancement factors ($\varepsilon_H$ = 21, $\varepsilon_{C\,CP}$ = 30), and very limited transfer of polarisation to the $^{17}$O of Mg($^{17}$OH)$_2$.

Despite the maximum $\varepsilon_{O\,CP}$ reported in Table 1 being for Mg($^{17}$OH)$_2$/BDPA/90:10 OTP-$d_{14}$:OTP, the corresponding $\Sigma^{+}_{O\,CP}$ value is still lower than the maximum $\Sigma^{+}_{O\,CP}$ values for $^{17}$O obtained with CE (using the same matrix). This is due to the much shorter $\tau_{DNP}$ in the CE system (~ 11 s) than that of the OE in OTP-$d_{14}$ (~ 31 s), allowing for more scans to be accumulated per unit time.

**Table 1**: A comparison of DNP enhancements measured at 18.8 T using CP Hahn Echo on Mg($^{17}$OH)$_2$ in a range of polarisation matrices (see SI). n/a indicates that these experiments were not run.

| Matrix | TCE | OTP | OTP / OTP-$d_{14}$ (50:50) | OTP / OTP-$d_{14}$ (90:10) | OTP / OTP-$d_{14}$ (95:5) |
|---|---|---|---|---|---|
| Cross Effect (1.3 %wt TEKPol) | | | | | |
| $\varepsilon_{O\,CP}$ | 14 | 6 | 12 | 11 | 12 |
| $\Sigma^{+}_{O\,CP}$ | 72 | 38 | 54 | 71 | 53 |
| Overhauser Effect (1.4 %wt BDPA) | | | | | |
| $\varepsilon_{O\,CP}$ | 5 | 2 | n/a | 17 | 3 |
| $\Sigma^{+}_{O\,CP}$ | 13 | 24 | n/a | 34 | 9 |

In conclusion, we have shown that it is possible to transfer the OE DNP enhanced polarisation of OTP doped with BDPA to the $^{17}$O spins of Mg($^{17}$OH)$_2$ hydroxides at 18.8 T with good efficiency by mixing both solids together. We have also demonstrated that despite the lower ε values obtained with CE, TEKPol/OTP and TEKPol/TCE provide time efficient signal enhancement. This has enabled large gain in absolute sensitivity permitting the challenging detection of natural abundance $^{17}$O NMR spectra. This study paves the way to a wider application of $^{17}$O DNP enhanced NMR at high magnetic field and its transposition to other quadrupolar nuclei in a variety of crystalline and amorphous inorganic materials with strong second-order quadrupolar broadenings hampering spectral resolution at low field.

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